Thermal Behaviors of Flame-Retardant Polycarbonates Containing Diphenyl Sulfonate and Poly(sulfonyl phenylene phosphonate)

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ABSTRACT: Potassium diphenyl sulfonate (SSK), poly-(sulfonyl phenylene phosphonate) (PSPPP), and their mixtures are proved to be effective flame-retardants for polycarbonates (PCs) by measuring the limited oxygen index values and UL-94 of blends. The flame-retardant systems are characterized by thermogravimetric analysis under dynamic conditions. The resulting data, together with the analysis of the activation energies, demonstrates that the additives accelerate thermodegradation, especially in the early stage, and different additives cause a different process in the final stage. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 882–889, 2003

Key words: flame-retardant; polycarbonate; thermogravimetric analysis

INTRODUCTION

Aromatic polycarbonates (PCs) are commercially exploited as engineering plastics in various fields because of their good properties. In recent years, they have been used for the exterior materials of office equipment. With the increasing concern for safety, effective flame-retardant PCs are needed.[1,2]

Aromatic sulfonates, such as sulfonic acids of aromatic ketones and heterocyclic sulfonic acids, are known as effective flame-retardant additives for PCs.[3–9] The investigations show that when present in catalytic amounts, aromatic sulfonates are capable of increasing the thermal degradation rate of PCs. As a consequence, the formation of a carbon layer at the burning surface is promoted.[10] In our experiments we used potassium diphenyl sulfonate (SSK) as a flame-retardant additive for PC. When the loading level of SSK was 0.5–1.0 wt %, the limited oxygen index (LOI) values reached 33.3–34.8. With the increase of the SSK content in the PC, its LOI values do not increase and actually decrease. It appears that 1.0 wt % SSK (S_1, where S is the sample and the subscript number is the weight percentage of SSK) made the PC reach a maximum LOI value. In other words, it is useless to increase the contents of SSK in order to obtain much higher LOI values. We discovered that when SSK was added to the PC with certain arylphosphonate compounds, for example, poly(sulfonyl phenylene phosphonate) (PSPPP),[11] the flame-retardancy of PC can be enhanced. The LOI value of a PC containing 0.5 wt % SSK and 4.5 wt % PSPPP ($S_{0.5+4.5}$, where the second subscript number indicates the weight percentage of PSPPP) was 36.8, and the transmission character of the flame-retardant PC was improved.

In an attempt to provide a basis to understand the effect of flame-retardant additives, some parameters of the combustion phenomenon, such as the LOI and UL-94, have been measured. Some kinetic parameters of thermal degradation were also evaluated to investigate the effect of flame-retardant additives by comparing the thermal behaviors of these two systems: PC/SSK and PC/SSK/PSPPP.

EXPERIMENTAL

Material

The PC (M_n = 28,000) was obtained from Changzhou Chemistry Company (Jiangsu, China). The SSK (mp = 152–154°C, T_d = 530°C) and PSPPP (mp = ~210°C; T_d = 405°C, M_n = 8000–9000) were provided by Weili Flame-Retardant Chemicals Co., Ltd. (Chengdu, China)

Blend preparation

The PCs were mixed with 0.5, 1, 3, and 5 wt % of fine dried SSK powders by tumbling the ingredients in a tumbler. The resulting mixtures were fed into a twin-

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TABLE I
Flame Retardancy of PC/SSK Mixture with Different Contes of SSK

	Samples				
	S_0	$S_{0.5}$	S_1	S_3	S_5
LOI (%)	26.3	33.3	34.8	33.6	33.0
UL-94 (rating)					
(3-mm thickness)	V-2	V-0	V-0	V-0	V-0

S_n The subsript numbers are the content of SSK added to the PC.

TABLE II
Flame-Retardancy of PC/SSK/PSPPP Mixture with Different Contents of SSK and PSPPP

	Samples					
	S_0	S_{0+5}	$S_{0.5+4}$	S_{1+4}	S_{3+2}	S_5
LOI (%)	26.3	31.9	36.8	35.2	32.9	33.0
UL-94 (rating)						
(3-mm thickness)	V-2	V-2	V-0	V-0	V-0	V-0

S_{n+m}, the subscript numbers are the contents of SSK and PSPPP added the to PC, respectively.

screw extruder operating at about 250°C, and the extrudates were comminuted into pellets.

Utilizing the same process, the PCs were mixed with 5 wt % SSK and PSPPP, whose respective proportions were 0:5, 0.5:4.5 ($S_{0.5+4.5}$), 1:4 (S_{1+4}), and 3:2 (S_{3+2}). The pellets were then injected into a mold at about 245°C and formed into standard test bars.

Measurements

The LOI value and UL rate measurements were performed according to ISO 4589-1984 and UL-94, respectively.

A DuPont 2100 thermal analyzer was used to determine the weight loss during the thermal degradation of pure PC and PC/SSK and PC/SSK/PSPPP mixtures. Experiments were carried out on 5 ± 0.25 mg of the samples under nitrogen at a flow rate of 50 mL/min and a furnace heating rate of 10°C/min up to 700°C.

The thermooxidation behavior was also studied on a DuPont 2100, which measured the sample weight loss as a function of the linearly increasing temperature. Sample weights of 5 ± 0.25 mg were used throughout the study at heating rates of 5, 10, 20, and 40°C/min. All experiments were performed in air at a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Flammability

The LOI values as a function of the SSK concentrations are shown in Table I. From Table I we can see that a small addition of SSK (0.5 wt %, $S_{0.5}$) causes a sensible LOI increment in the PC, and the LOI value of the PC containing 1.0 wt % SSK seems to reach the maximum. When the content of SSK was increased beyond 1.0 wt %, the flame-retardant character of the mixtures became poor, which means that a further increment of the LOI values of PC cannot be achieved by increasing
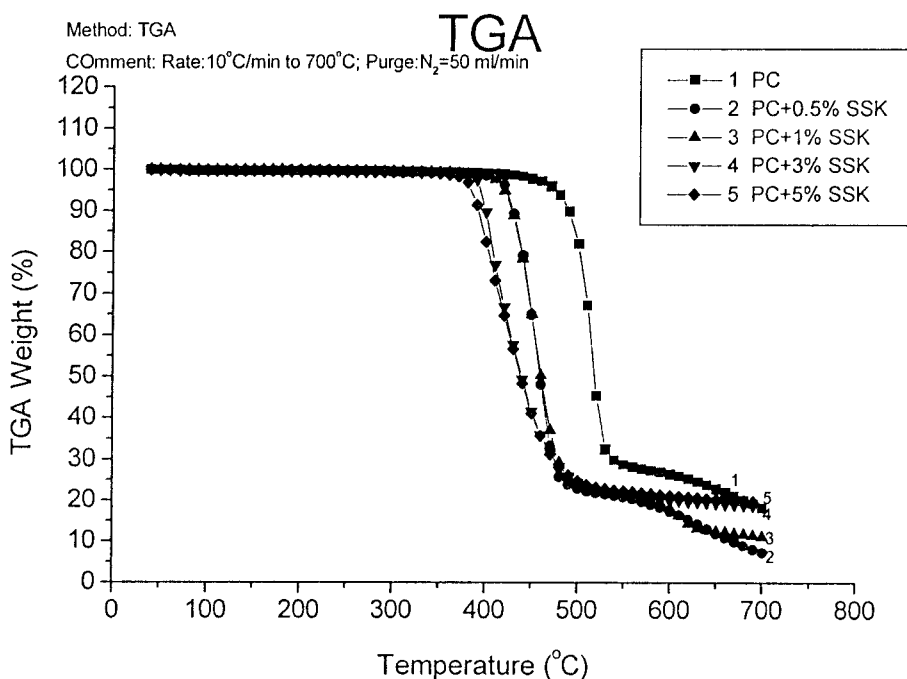
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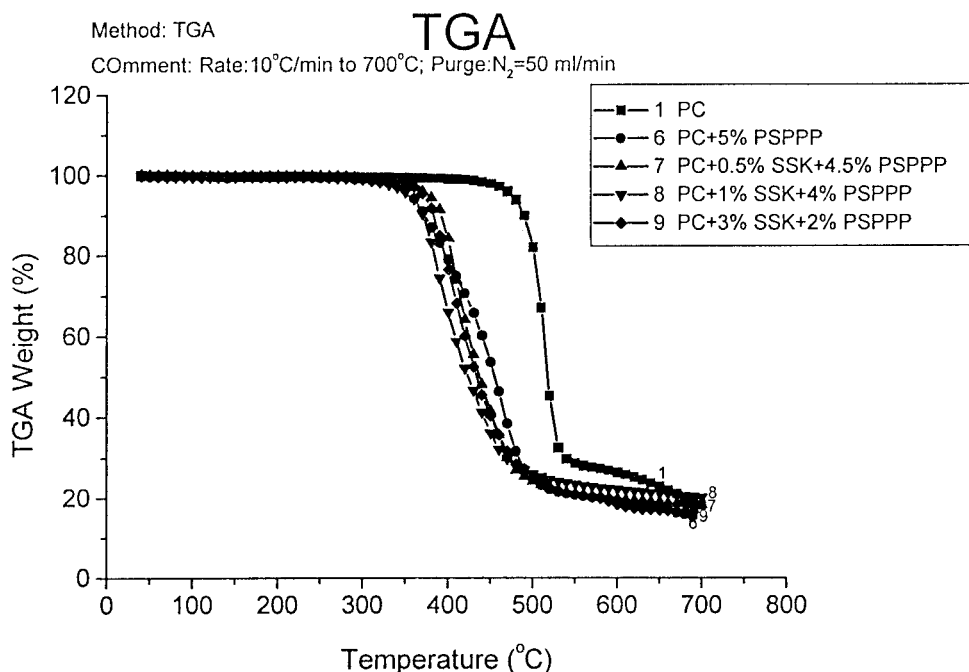**Figure 1** The TGA curve of the PC/SSK mixture.

Figure 2 The TGA curve of the PC/SSK/PSPPP mixture.

the content of SSK. Table II shows the LOI results of simultaneously adding the SSK and PSPPP to the PC. It is evident that the addition of 4.0 and 4.5 wt % PSPPP to PC can cause the increment of the LOI values. The LOI value is 36.8 when 0.5 wt % SSK and 4.5 wt % PSPPP are added to the PC, which means that SSK and PSPPP have a synergistic effect on the flame-retardancy of PC.

Thermal analysis

The thermogravimetric analysis (TGA) curves of all samples are depicted in Figures 1 and 2. The thermal stabilities of the components that make up these samples are similar. The flame-retardants SSK and PSPPP have high decomposition temperatures (>400°C). As evidenced from Figures 1 and 2, SSK and PSPPP cause thermal destabilization and the rate of weight loss increases as the amount of flame-retardant additives increases. SSK and PSPPP widen the temperature range of PC decomposition, which is favorable for reducing the amount of combustible volatile products within the range of combustible temperatures of PC.

Comparing Figure 1 and Figure 2, we find that the residues of the two systems at 700°C are different. These data are available from Table III. In a comparison of $S_{0.5}$ with $S_{0.5+4.5}$, there are 11% more residues of the latter than of the former. The same case can be observed between S_1 and S_{1+4}. In fact, the LOI values of $S_{0.5+4.5}$ and S_{1+4} are higher than those of $S_{0.5}$ and S_1, respectively. It seems that the

higher LOI values are relative to the larger residues. It is apparent that the residues at 700°C are the results of charring, which suggests that the addition of PSPPP can cause the quantitative increase of the carbon layer, even if present in a small amount. This result will be further verified in the following discussion.

The TGA and derivative TG (DTG) curves of samples in air and in N_2 are depicted in Figures 3 and 4, respectively. It is evident that the samples of the two systems undergo a different thermal degradation because of the effect of oxygen. This means that there is a more complex degradation mechanism in air than in N_2.

The TGA and DTG curves of samples of pure PC (S_0), S_5, and S_{3+2} at different heating rates are depicted in Figures 5–10. The kinetic parameters of thermal degradation can be used to characterize the thermal stability, and the activation energy (E_a) can be consid-

TABLE III
Residues of Thermal Degradation at 700°C

Samples	Residues at 700°C (%)	LOI (%)
$S_{0.5}$	7.27	33.3
S_1	11.06	34.8
S_3	18.67	33.6
$S_{0.5+4.5}$	18.18	36.8
S_{1+4}	20.30	35.2
S_{3+2}	16.48	32.9

S_n, S_{n+m}, the subscript numbers are the contents of SSK and the contents of SSK and PSPPP, respectively.
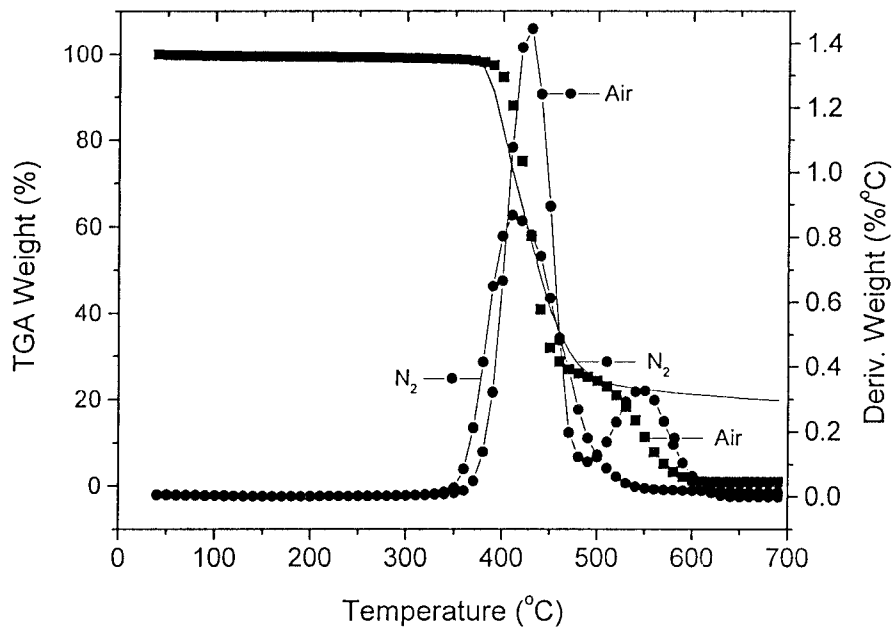
Figure 3 The TGA and DTG curses of PC with 5 wt % SSK (S_5) under N_2 and air.

ered as a semiquantitative factor. The peak rate temperatures determined at different heating rates allowed the activation energy to be determined by the Kissinger method.[12,13] We applied this approach to our data and calculated the values presented in Table IV. According to the DTG curves, the two stages of decomposition were studied with the Kissinger kinetic analysis.

The Kissinger expression is as follows:

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln[n(1 - \alpha_{max})^{n-1}]\right\} - \frac{E}{RT_{max}} \quad (1)$$

where β is the heating rate, T_{max} is the temperature of the peak rate, A is the absorbance, R is a gas constant, and α is the conversion rate.

Plotting the natural logarithm of β/T_{max}^2 against the reciprocal of the absolute temperature $(1/T_{max}^2)$, the
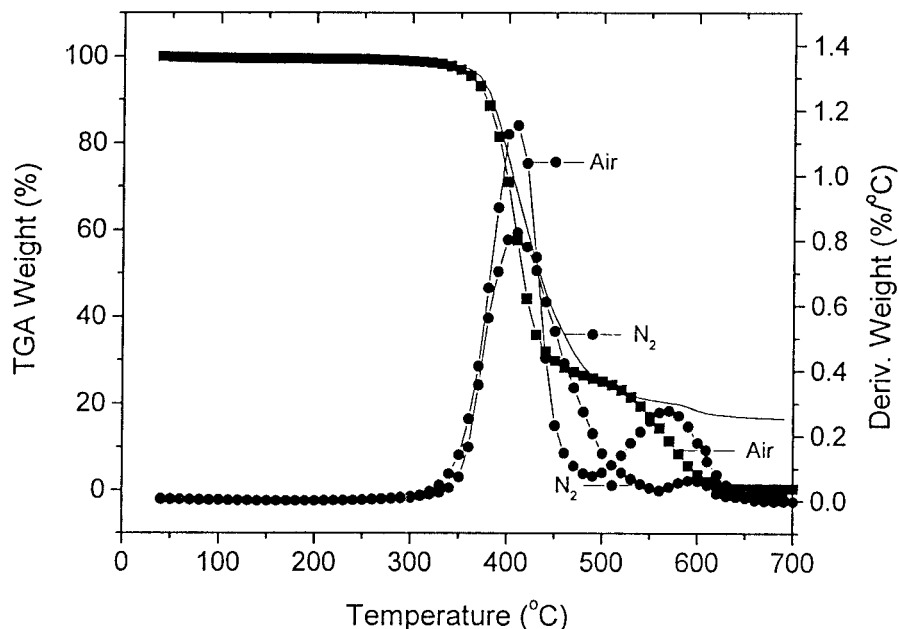

Figure 4 The TGA and DTG curves of PC with 3 wt % SSK and 2 wt % PSPPP (S_{3+2}) under N_2 and air.
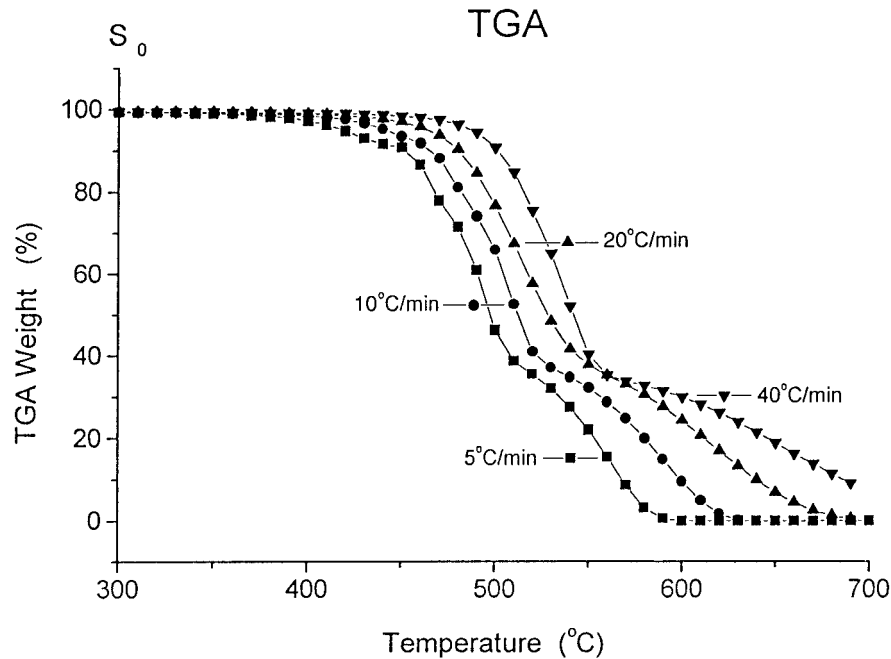
TGA

S₀

Figure 5 The TGA curves of PC at different heating rates.

slope of the resulting line is given by $-E/R$, which allows the value of E to be obtained.

Clearly, for the main weight loss region (the first stage), there are many differences in the activation energy between S_3 or S_{3+2} and S_0, but the two flame-retardant PC systems S_3 and S_{3+2} show little difference. That is to say, the flame-retardant additives cause the same effect on the PC. The E_a value of PC with flame-retardant additives is much lower than

pure PC. This suggests that the addition of flame-retardants to PC accelerates the thermal degradation of PC in the first stage. In the second weight loss region (the second stage), the activation energy of S_5 is similar to that of S_0 but different for S_{3+2} and S_0. That is to say, the main differences in the activation energies between S_5 and S_{3+2} were associated with the second weight loss region where the oxidation of the char plays a significant role. The activation energy of
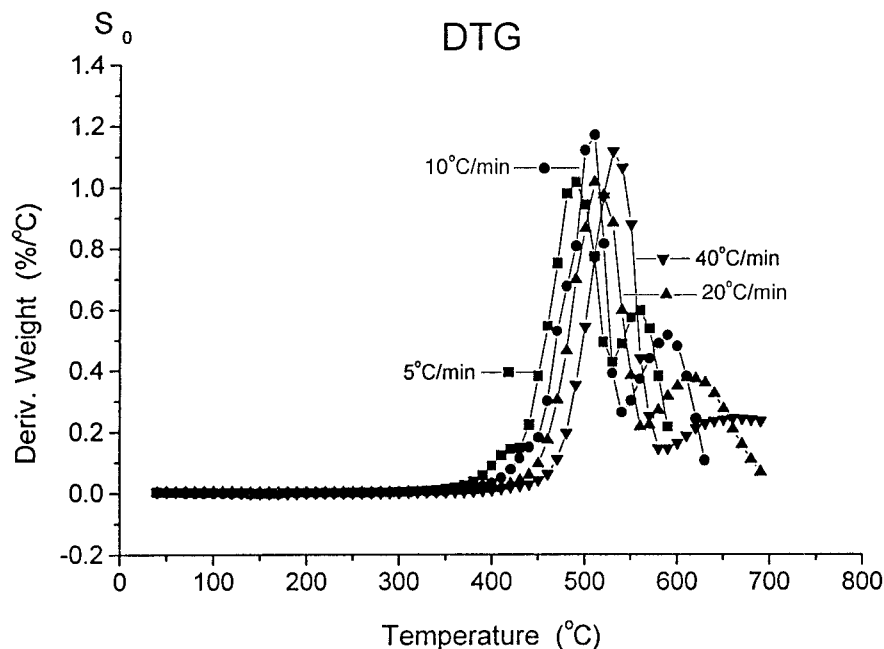
DTG

S₀

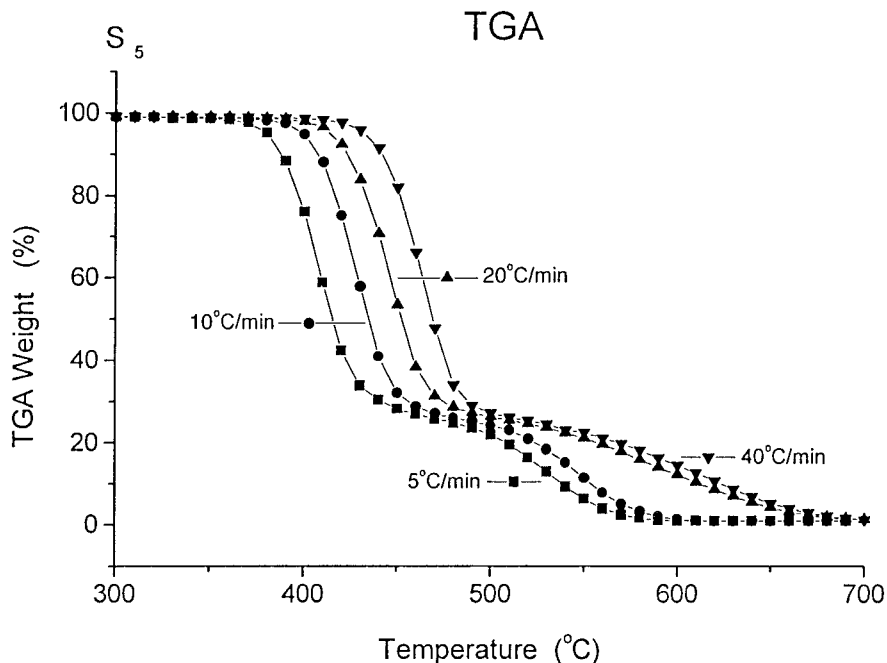**Figure 6** The DTG curves of PC at different heating rates.

Figure 7 The TGA curves of PC with SSK at different heating rates.

S_{3+2} is much higher than that of S_5. It shows higher thermal stability than S_5 in the second stage. This result corresponds to high residues at 700°C when PSPPP was used. However, the Kissinger data are of limited value in that they only provide information at the peak rates.

More informative kinetic data are obtained by the application of the Flynn technique.[14] In this approach

the activation energy for the degradation process is calculated from the following expression:

$$\log\beta = \log AE/g(\alpha)R - 2.315 - \frac{0.457}{RT}E \qquad (2)$$

The log of the heating rate (β) is plotted versus the reciprocal of the absolute temperature ($1/T$) for a fixed
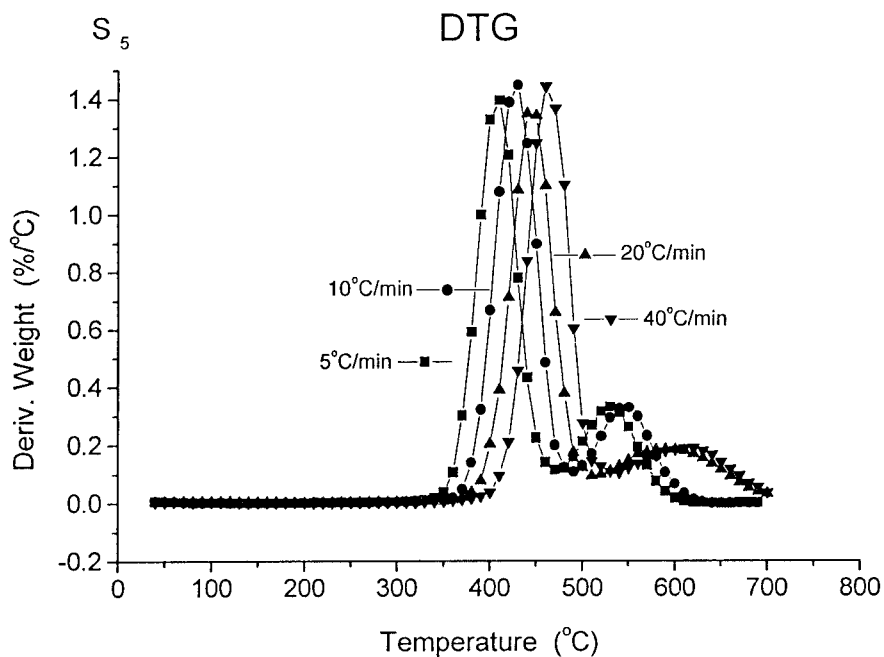

Figure 8 The DTG curves of PC with 5 wt % SSK at different heating rates.
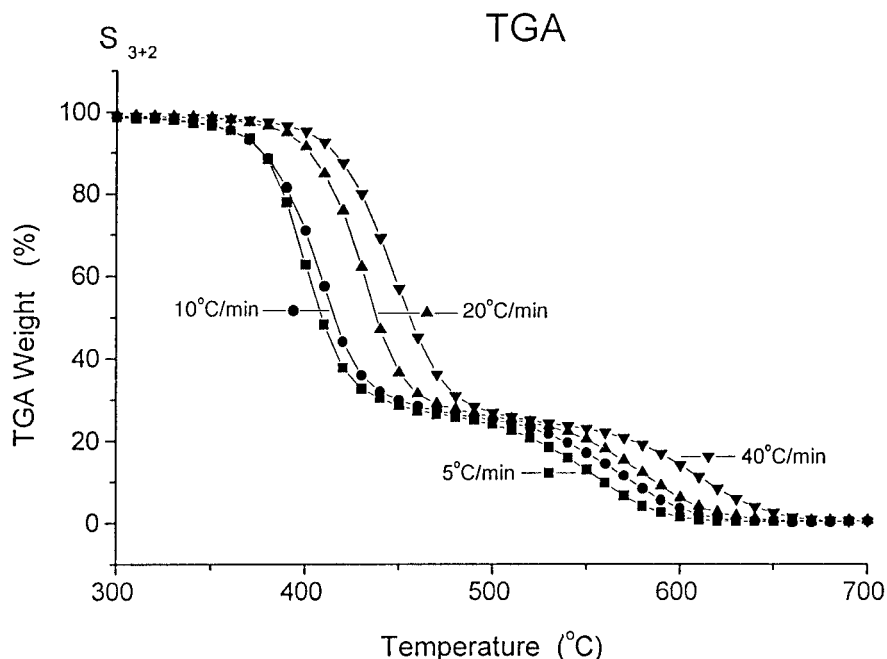
TGA

Figure 9 The TGA curves of PC with 3 wt % SSK and 2 wt % PSPPP at different heating rates.

degree of conversion (α). The slope of the resulting line is given by $-0.457E/R$, from which the value of E can be obtained. These data for the activation energies are summarized in Table V.

From Table V we can see that all the samples tend to show three zones of activation energies. In the early stage the loss of the light degradation compounds, such as carbon dioxide, occurs. Pure PC (S_0) completed this stage before 10% weight loss, but flame-retardant PC could only be completed before 3%

weight loss. This proves that the additives show their effects during this stage by accelerating the evolution of incombustible gas (carbon dioxide). After the early stage, the E_a values of flame-retardant PC rise as degradation proceeds, remaining constant up to 80%, which means that the stabilities of the intermediate products are rather similar. The pure PC, whose E_a values are higher than those of flame-retardant PC, also shows an increase, suggesting that the pure PC has better thermal stability than flame-retardant PC in
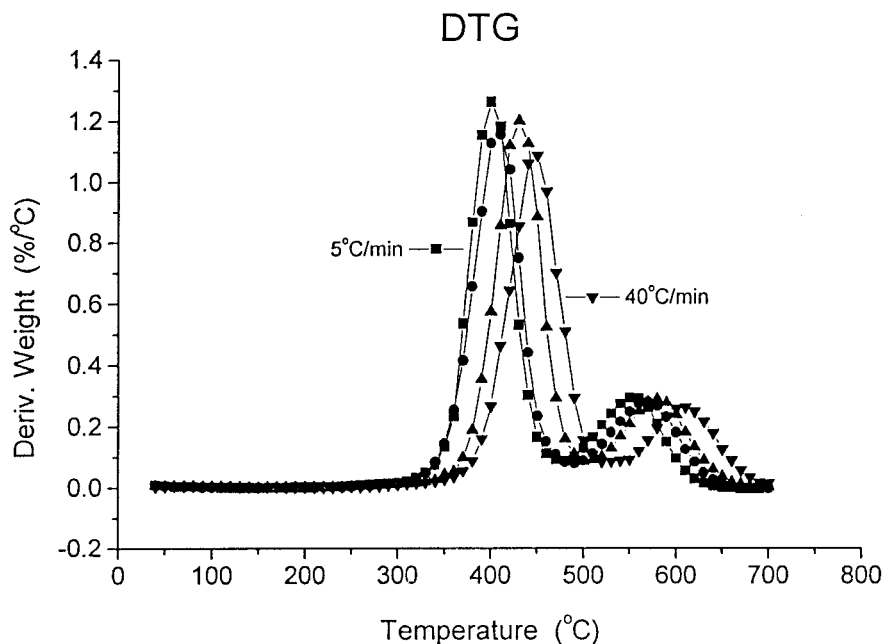
DTG

Figure 10 The DTG curves of PC with 3 wt % SSK and 2 wt % PSPPP at different heating rates.

this stage. In other words, the additives cause faster degradation of the PC. Because of the different components of the flame-retardant additives, S_5 and S_{3+2} are distinguished in the final stage (80–90%) of the degradation process. The results are similar to those from the Kissinger method. For S_5 the process is also accelerated; on the contrary, it is slowed down for S_{3+2}. During the main weight loss stage, the flame-retardant PC has lower activation energies than pure PC.

TABLE IV
Activation Energies (E_a) Calculated According to Kissinger Method

Sample	First Stage	Peak Temp. (°C)	Peak Rate (%/min)	E_a (kJ/mol)
S_0	β (°C/min)			205.03
	5	494.00	1.016	
	10	508.26	1.119	
	20	514.90	1.014	
	40	539.27	1.116	
S_5	β (°C/min)			154.66
	5	408.96	1.393	
	10	432.55	1.446	
	20	445.72	1.347	
	40	464.37	1.442	
S_{3+2}	β(°C/min)			165.06
	5	400.90	1.262	
	10	411.98	1.154	
	20	432.27	1.198	
	40	448.45	1.086	
	Second Stage			
S_0	β (°C/min)			108.52
	5	563.75	0.5973	
	10	592.64	0.5144	
	20	616.58	0.3732	
	40	660.00	0.2389	
S_5	β(°C/min)			98.97
	5	530.61	0.3298	
	10	546.68	0.3257	
	20	602.37	0.1825	
	40	622.65	0.1880	
S_{3+2}	β(°C/min)			217.50
	5	558.95	0.2908	
	10	573.35	0.2787	
	20	581.44	0.2858	
	40	606.12	0.2595	

TABLE V
Kinetic Parameters by Flynn Method

Conversion Rate (%)	E_a (kJ/mol)		
	S_0	S_5	S_{3+2}
1	107.01	104.10	109.77
3	118.28	145.86	162.59
5	117.62	153.00	175.72
10	187.57	152.64	184.74
15	192.28	152.38	182.64
30	203.67	152.03	178.23
50	204.80	152.74	179.58
65	202.50	152.47	181.55
80	108.86	105.92	218.32
90	111.60	107.37	221.83

CONCLUSION

Flame-retardant additives such as SSK and SSK/PSPPP give PC high flame-retardancy. The flame-retardant additives accelerate the thermal degradation of PC, especially in the early stage, which can be concluded from the kinetic measurements of the weight-loss decomposition rate. Both SSK and PSPPP have important roles, but their effects are quite different, especially in the final stage. The flame-retardant action of SSK and PSPPP on PC is synergistic.

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